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USE OF RADIATION IN PREPARATIVE CHEMISTRY

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Cleveland, Ohio
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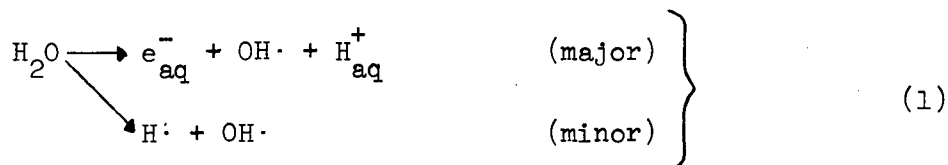
Lewis Research Center

SUMMARY

This paper represents a summary and updating of our previous work on the use of radiation chemistry for the preparation of pure materials. We have been chiefly concerned with the reduction of metal salts in solution to the free metal using 2 MeV electrons. Metals deposited from aqueous solution are copper, silver, zinc, cadmium, thallium, tin, lead, antimony, iron, nickel, cobalt, and palladium. Dry organic solvents have been evaluated for the deposition of metals based on a study involving deposition of antimony from solutions of antimony (III) chloride. The use of organic liquids for the preparation of anhydrous metal halides is also presented. Reaction mechanisms for both organic liquids and aqueous systems are discussed.

INTRODUCTION

Pulse radiolysis of aqueous solution coupled with high speed spectroscopy has enabled investigators to identify short lived species and to obtain kinetic data for fast reactions. An important discovery is that a major reducing species in irradiated aqueous systems is the relatively long lived hydrated electron (ref. 1). The action of ionizing radiation (e.g., high energy electrons) on water may be represented as follows.



where

e_{aq}^- hydrated electron
 $\text{H}\cdot$ atomic hydrogen
 $\text{OH}\cdot$ hydroxyl radical
 H_{aq}^+ hydrated proton

Every 100 electron volts of radiation energy produces about four hydrated (solvated) electrons. Therefore, a single 1 MeV electron from an irradiation source would produce over 10^4 hydrated electrons, e_{aq}^- .

Addition of an OH radical scavenger (e.g., methanol) which reacts rapidly with the oxidizing $\text{OH}\cdot$ but slowly with the reducing $\text{H}\cdot$ and e_{aq}^- generates an overall reducing system. In a similar fashion, addition of a scavenger for $\text{H}\cdot$ and e_{aq}^- (e.g., hydrogen peroxide) results in an oxidizing system due to the presence of excess of $\text{OH}\cdot$ radicals. The specific rate constants for the reaction of these species with many compounds and ions have been compiled by Anbar and Neta (ref. 2).

We have been chiefly but not solely concerned with the reduction of metal salts in solution to the free metal by 2 MeV electron irradiation. Our work has been essentially a scale up of the pulse radiolysis process. In other words, we have been preparing macro quantities of products by use of continuous high intensity radiation. This paper summarizes and brings up to date our previous more detailed reports (refs. 3 to 6).

METAL OBTAINED FROM THE RADIOLYSIS OF AQUEOUS SYSTEMS

Table I lists the yields of the 12 metals we have prepared by electron irradiation of their aqueous salt solutions. The yield is first expressed in terms of $n \cdot G(M)$ where n is the valence change that occurs when the metal ion is reduced to the metal and $G(M)$ is the number of metal atoms produced for 100 eV energy. The yield is also expressed in grams per kilowatt-hour. For a valence change of two, an $n \cdot G(M)$ value of 1 is equivalent to about 0.2 mole of metal product per kilowatt-hour of energy into the solution.

In most cases metals produced radiochemically from aqueous solution deposit as fine powders. In the electron microscope photograph (fig. 1) the silver particles appear as a self sintered agglomerate of fine crystallites of sizes down to 0.1 micron. The metal powders, especially the more active metals are sensitive to atmospheric oxidation. The soft metals, cadmium, tin, and particularly lead form macro sponge-like conglomerates. When formed by irradiating a solution of a weak electrolyte (e.g., lead acetate) some of the lead is colloidal. In such a solution a lead mirror deposits on the glass reaction vessel. No colloidal lead is formed from a solution of a strong electrolyte (e.g., lead perchlorate or a basic solution containing lead acetate).

Inherent characteristics of the radio-chemical method lead to the production of high purity metals. Deposition of metals occurs at low enough temperatures where contamination due to diffusion of container material or reaction with the environment is minimized. Also, the product is isolated as a precipitate; the reactants and unwanted reaction products remain in solution. And finally, easily purified metal salts may be used.

A detailed chemical analysis was not done for each metal; however, in each case X-ray diffraction showed that only the metal was present. Samples of silver, copper, and nickel were all found to be 99.9+ percent pure by chemical analysis. The emission spectrographic analysis of the silver prepared from laboratory reagents (used without additional purification) is shown in table II. Also shown is a qualitative comparison of a copper metal sample (prepared from aqueous copper sulfate containing methanol) with spectrographic grade copper oxide. For both the Ag and Cu some contaminants such as Al, B, and Ca probably originated from the glass apparatus.

Antimony and some anhydrous lower valence metal halides were prepared using dry organic liquids as solvents. Such materials are fine powders which are sensitive to atmospheric oxidation. Many vacuum dried antimony powder samples were pyrophoric; thus it was necessary to vacuum sinter these samples before exposing them to the atmosphere.

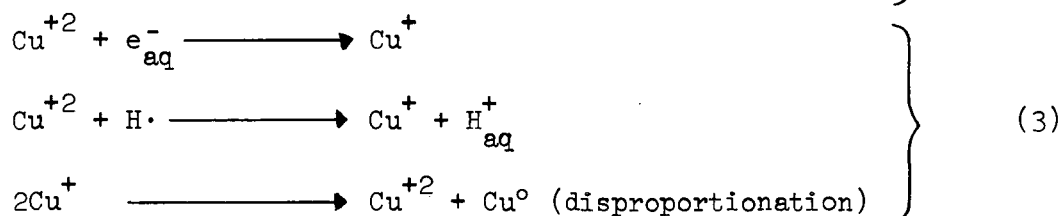
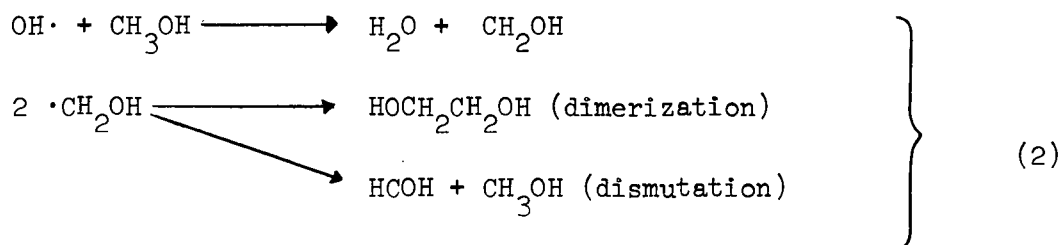
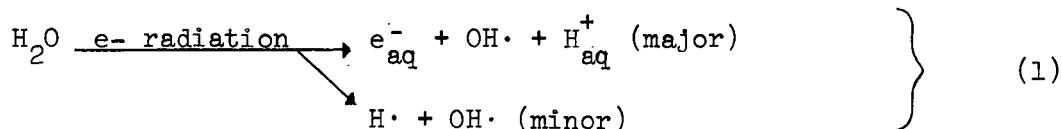
GENERAL PROCEDURE

The glass reaction vessel (fig. 2) and the general procedure have been described previously (refs. 3 to 6). To summarize, the solution (about 500 cc) containing the metal salt and scavenger (if aqueous) is agitated in the vessel during irradiation by passing an inert gas through a glass frit at the base of the reaction vessel. The contents are kept at about 20° C during irradiation by immersing the reaction vessel in a water bath. The electron beam is furnished by a Dynamitron accelerator capable of supplying accelerating potentials between 0.5 and 3.0 million volts and a controllable beam current capability up to 10 milliamperes. The duration of the average run is between 1 and 2 hours. The dose (coulombs) is obtained from a beam current integrator. The product yield, $n \cdot G(M)$ is found to be essentially independent of electron accelerating voltage between 0.5 and 2.5 MeV. A selection of 2 MeV for the accelerating voltage for all runs proved to be convenient for the general operation of the experiment. The penetration of these electrons is about 1 centimeter; the diameter of the beam is about 4 centimeters.

After irradiation, the insoluble product deposited from aqueous solution is removed by centrifuging and washed thoroughly with water. The wet powder is then suspended in acetone, filtered on a fritted glass filter and dried at room temperature overnight. The tared filter containing the metal powder is further dried at about 70° C for 2 hours and weighed. The relatively low drying temperature is used to prevent undue atmospheric oxidation of the metal powder. Metal samples used for analysis were vacuum dried at 100° C instead of being dried in air. Preparations of anhydrous and pyrophoric materials from organic solvents require special isolation techniques.

MECHANISM IN AQUEOUS SYSTEMS

In general, the reduction of a metal salt in aqueous solution proceeds according to the radical scavenging mechanism. Using Cu as the metal to be deposited and methanol (CH_3OH) as the scavenger for OH radicals, the mechanism is illustrated by the following equations.



In order for free metal to form from a solution of its divalent ion, the monovalent metal ion must be unstable with respect to disproportionation. The existence of several monovalent metal ions has been identified spectroscopically by pulse radiolysis. These ions have been found to decay by second order kinetics suggesting a disproportionation reaction as indicated in the mechanism (ref. 7).

Allan and Beck (ref. 8) from their results on the radiolysis of aqueous solutions (2-propanol and nitrous oxide) report a maximum yield for the decomposition of water $G(-\text{H}_2\text{O}) = 4.50 \pm 0.10$ atoms per 100 eV for 2.5 MeV electrons. Then $G(-\text{H}_2\text{O}) = G(\text{red}) = G(\text{ox}) = 4.5$ atoms per 100 eV. If all of the reducing species (e_{aq}^- and $\text{H}\cdot$) in irradiated water are used in reducing the metal salt to free metal, the maximum metal yield $n \cdot G(\text{M})$ would equal this value. In terms of electron beam power (beam current times beam voltage) the maximum yield of metal from its divalent ion in aqueous solution would be 0.85 moles per kilowatt-hour.

SELECTION OF METAL SALT

In the selection of the proper salt for the deposition of metals, consideration must be given to possible reduction of the anion; thus

for maximum metal yield only those anions may be used whose reaction rate with $H\cdot$ and especially e_{aq}^- is low. These anions include sulfate ($SO_4^{=}$), cyanate (CNO^-), thiocyanate (CNS^-), perchlorate (ClO_4^-), azide (N_3^-), acetate (CH_3COO^-), formate ($HCOO^-$), and the halides (F^- , Cl^- , Br^- , I^-) (ref. 2).

Table III gives the product and yield when aqueous solutions of various copper salts (different anions) are irradiated. Equally good copper yields are obtained by using either $CuSO_4$ or $Cu(ClO_4)_2$. Solutions of $Cu(CH_3COO)_2$ and $CuCl_2$ precipitate Cu_2O and Cu_2Cl_2 , respectively, and no free copper is formed. Such yields involving the Cu^{+1} ion illustrate the stepwise reduction of Cu^{+2} by e_{aq}^- and $H\cdot$. In the irradiation of salts such as $Cu(CH_3COO)_2$ and $CuCl_2$ the monovalent copper species is formed because of its precipitation as a stable compound. No copper forms on irradiation of ammoniacal $CuSO_4$ because of the formation of the monovalent copper-ammonia complex ion which is stable toward disproportionation. As expected low copper yields are obtained from solutions of copper nitrate because of the competition of nitrate ion for the e_{aq}^- and $H\cdot$ resulting in the reduction of the nitrate ion.

SELECTION OF SCAVENGERS

Table IV shows the effect of various organic additives on the yield of copper from 0.2 molar $CuSO_4$. Good copper yields, close to the proposed maximum, $n\cdot G(Cu)$ of 4.5, are obtained using a variety of organic additives with easily oxidizable functional groups. These groups which apparently are good scavengers for $OH\cdot$ usually contain hydrogen atoms on the carbon atom in the functional group. Such compounds include primary alcohols, secondary alcohols, polyhydroxy alcohols and cyclic ethers. Poor yields are obtained with pyrogallol although it is readily oxidized to a quinone. The failure of pyrogallol in this respect is attributed to the fact that both pyrogallol or its oxidation product, a quinone, also scavenge the e_{aq}^- and $H\cdot$. No copper is obtained with the acetylenic alcohol, 2-propyn-1-ol which suggests that the triple carbon to carbon bond has an inhibiting effect.

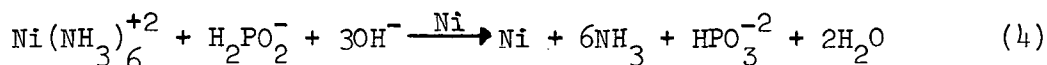
A second set of experiments was conducted on the deposition of the more active metal, nickel, from ammoniacal nickel sulfate. Examination of various organic additives (table V) shows that the highest $n\cdot G(Ni)$ is obtained with 2-propanol, the only secondary alcohol tested. Low yields are obtained with primary alcohols and the cyclic ether, tetrahydrofuran. Practically no nickel formed with the rest of the organic additives.

The comparatively high yield with the secondary alcohol, 2-propanol, is thought to be due to the formation of the oxidation product, acetone,

which being a ketone is stable toward further oxidation and does not form condensation products with ammonia.

In contrast oxidation of primary alcohols by OH radicals produces aldehydes which form condensation products with ammonia. These nitrogen containing organic compounds probably scavenge the reducing species in irradiated water (e_{aq}^- and $H\cdot$) thus competing with $Ni(NH_3)_6^{+2}$ for these species. The overall effect, of course, would be to lower the yield of nickel metal.

The unusually high nickel yield in solutions containing hypophosphite ion is attributed to an autocatalytic mechanism. Small amounts of nickel originally produced by the scavenging mechanism catalyze the following reaction.



The nickel produced according to this equation catalyzes the formation of even more nickel through the same reaction. As would be expected, the autocatalytic mechanism results in a higher yield of nickel than the radical scavenging mechanism. Because $Ni(NH_3)_6^{+2}$ is reduced by hot aqueous NaH_2PO_2 without radiation, hypophosphite solutions were maintained at 56°C during exposure to the electron beam.

The effect of the different scavenger systems upon yields of other metals can be seen in table VI. These yields in terms of $n \cdot G(M)$ are in most cases given for three different aqueous solutions as indicated in the three columns of the table. The first solution contained the metal salt and methanol as the OH radical scavenger. In some cases a small amount of acid corresponding to the anion of the metal salt was added to effect solution. The second and third aqueous systems were alkaline and used 2-propanol and sodium hypophosphite (NaH_2PO_2), respectively, as the additive to scavenge OH radicals. It is apparent from table VI that some metals are more easily prepared from neutral or acid solutions while others are more readily formed in alkaline solution. This fact is related to their individual chemistry.

It is interesting to note that the autocatalytic mechanism involving the metal and hypophosphite ion appears to be specific for nickel. Only for nickel is the yield ($n \cdot G(Ni) > 20$) substantially higher than the proposed maximum yield of 4.5 for the radical scavenging mechanism. For other metals the hypophosphite ion simply functioned as a scavenger for OH radicals. Because of the chemical similarity between nickel and cobalt, the low cobalt yield in hypophosphite solution was unexpected.

EFFECT OF CONCENTRATIONS

Figure 3 shows the effect of CH_3OH and CuSO_4 concentrations on $n \cdot G(\text{Cu})$. The yield of copper remains fairly constant $n \cdot G(\text{Cu}) = 4.0$ to 4.6 over a wide CH_3OH concentration range: 0.2M to about 6.8M. Between these concentrations, CH_3OH appears to be an efficient scavenger for $\text{OH} \cdot$.

Above 5M CH_3OH the copper yield drops off. This drop off is likely due to a deficiency of water concentration because of dilution with methanol. The yield also gradually falls off below 0.2M CH_3OH ; we found a value as low as 0.68 at 0.01M CH_3OH .

The fast reaction rate of Cu^{+2} with $\text{H} \cdot$ and especially e_{aq}^- (ref. 2) would lead one to predict the lack of a strong dependence of yield on CuSO_4 concentration. This is indeed the situation which is found in figure 3. This lack of dependence on Cu^{+2} ion concentration permits almost complete removal of this ion from solution. Beginning with an initial CuSO_4 concentration of 0.025M as indicated on figure 3, copper was for practical purposes completely removed (final Cu^{+2} concentration 0.001M) with a yield of 2.5.

SELECTIVE DEPOSITION AND CODEPOSITION OF METALS

The composition of metal deposited from a solution containing two or more metal ions depends on many factors such as the reaction rate of metal ions with e_{aq}^- and $\text{H} \cdot$, the kinetics of the disproportionation reaction, and the thermodynamics involved in the system. The influence of thermodynamics is illustrated in the preferential deposition of copper from an acid solution containing equal molar concentrations of Cu^{+2} and Ni^{+2} and the preferential deposition of cadmium from an alkaline solution containing equal concentrations of both Cd^{+2} and Zn^{+2} (table VII). In contrast some metals can be codeposited as illustrated in table VIII; here the codeposition of cobalt and nickel from ammoniacal Co^{+2} and Ni^{+2} is shown to depend upon the relative concentrations on the two metal ions.

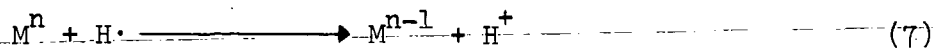
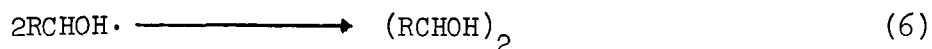
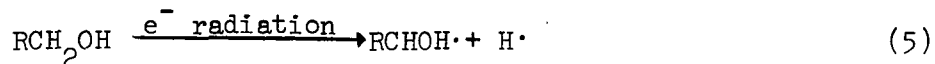
PREPARATION FROM ORGANIC LIQUIDS

Active metals, those which reduce water, and anhydrous compounds are best prepared for dry organic liquids. To evaluate various organic liquids for this purpose, antimony (III) chloride (SbCl_3) was selected as the metal salt because of its solubility in a wide variety of organic liquids and also because of the relative convenience in handling antimony metal.

Table IX gives the yield and in some cases the purity of antimony deposited from a variety of common organic liquids. Greatest yields and highest purity of antimony are obtained using primary alcohols, while the use of less polar liquids (aromatic hydrocarbons) results in lower yields and metal of poor quality. Because of the sensitivity of these powders to atmospheric oxidation, as mentioned previously, the antimony powder must be vacuum sintered before exposing to the atmosphere. The results in table IX are for the sintered metal. The contamination of the antimony in some systems is attributed to adsorbed organic material on the fine metal powder; this organic material carbonizes during the sintering operation. A more detailed account of our work on the radiation induced preparation of antimony from organic solvents has been previously reported (ref. 6).

Taking into account the reaction products from the radiolysis of aliphatic alcohols, McDonnell and Newton (ref. 9) claim that the principal bond rupture is at the carbinol carbon atom. Our results show that high antimony yields are obtained with those alcohols (primary and secondary) which have at least one hydrogen atom on the carbinol carbon. In contrast poor yields result from the tertiary alcohol 2-methyl-2-propanol with no hydrogen on this carbinol carbon atom. This suggests that hydrogen atoms play a significant part in the reduction process during the irradiation of organic liquids. It is true that solvated electrons have been observed in pulse irradiated primary and secondary alcohols, $G(e_{sol}^-) = \text{about } 1.0$ (ref. 10). However, the yield of antimony in these liquids can be considerably greater than this ($n \cdot G(\text{Sb}) = 2.4$) indicating that the solvated electron is not the only reducing species. Unlike the lack of dependence on $n \cdot G(\text{Cu})$ on copper ion concentration in aqueous solution, the yield of antimony ($n \cdot G(\text{Sb})$) deposited from tetrahydrofuran solution increases with SbCl_3 concentration from 0.55 at 0.1M SbCl_3 to 3.7 at 1.0M SbCl_3 as shown in figure 4. This trend is also observed in methanol solution. At 0.25M SbCl_3 the yield ($n \cdot G(\text{Sb})$) is 2.4 while at 0.5M SbCl_3 this yield is 3.6. The dependence of yield on concentration implies a relatively slow reaction rate of the tri-valent antimony with the reducing agent. Slow reaction of this type are more characteristic of hydrogen atoms than solvated electrons.

The proposed mechanism for the reduction of a metal in oxidation state n to oxidation state $n-1$ is:



where R is any organic group, the irradiated liquid is a primary alcohol, and the hydrogen atom is the reducing species.

Besides the use of organic liquids for the deposition of metals, they may also be used for the synthesis of anhydrous salts, in particular, metal halides. This is accomplished by irradiating a solution of a metal halide where the metal ion is in a higher oxidation state than it is in for the metal halide to be prepared. In general the higher valence halide is more soluble in organic liquids than the lower valence halide. Thus on irradiation the original metal halide is reduced to the more insoluble halide which is then easily separated as a precipitate. Examples of these syntheses are shown in table X.

CONCLUDING REMARKS

Our work is only a beginning with respect to the potential use of radiation chemistry for synthesis in liquid systems. This report covers a few useful preparations involving reducing reactions. In aqueous systems alone, selective use of any one of the three species formed in irradiated water, $H\cdot$, e_{aq}^- , and $OH\cdot$ could be accomplished by proper selection of scavengers. Oxidations could be done with OH radicals. Reductions involving attack of an electron deficient area of an organic molecule may be achieved by the solvated electron and other specific reductions could make use of hydrogen atoms.

Liquid radiochemical reactions have at least three characteristics that are desirable for the preparation of high purity materials. These are (1) it is a low temperature method, (2) the solid product precipitates from the liquid phase and (3) a wide choice of liquid systems may be employed.

Reactions may be carried out at room temperature or below. Low temperature retards the reaction and diffusion of container materials and environmental gas with the product. It enables appropriate selection of a container material to avoid contamination of the product by specific undesirable impurities.

The product separates as a solid from a liquid phase which allows a simple procedure for isolation of the product. Reactants and unwanted reaction products remain in solution.

A wide choice of liquid systems may be used in radiochemical preparations. For example, solutions are not limited to electrically conducting solutions as is the case for an electrolytic process.

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TABLE I. - YIELDS OF 12 METALS

Metal	n·G(M)	Yield, grams per kilowatt· hour
Copper	4.4	52
Silver	3.6	145
Zinc	.28	3.4
Cadmium	1.8	38
Thallium	^a .79	60
Tin	^a .20	4.4
Lead	3.2	124
Antimony	^a 2.7	41
Iron	^a .001	.01
Nickel	^a 1.7	19
Cobalt	^a .6	6.6
Palladium	4.7	93

^aPrepared from alkaline solution.

TABLE II. - SPECTROGRAPHIC ANALYSES

[Emission Spectrographic Analysis of Silver Deposited Radiochemically from Aqueous

0.1M AgClO_4 , 1M NH_3 , 1M 2-PROPANOL.]

Contaminant	Al	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Ni	Si	Sn	Sr	Ti	V	Zn
PPM	5	2	<5	2	1	1	0	0.5	0.5	1	1	0.5	0	0.5	<0.3	<1

Qualitative emission spectrographic analysis of copper deposited radiochemically from aqueous 0.5M CuSO_4 , 2M methanol, 0.5M H_2SO_4 and the same analysis of spectrographic grade 5N+ copper oxide.

Contaminant	Ag	Al	As	B	Be	Bi	Ca	Co	Cr	Fe	Ga	Mg	Mn	Mo	Na	Nb	Ni	Pb	Sb	Si	Sn	Ta	Ti	V	W	Y	Zn	Zr
Our Cu	--	T	--	VW	--	--	FT	--	FT	FT	--	T	--	--	--	--	FT	FT	--	VW	--	--	--	--	--	--	--	--
Spectrographic copper oxide	FT	FT	--	--	--	T	W	--	W	VW	--	FT	W	T	--	--	VW	T	--	T	T	--	--	--	--	--	--	--

Symbol	Meaning	Minor Constituent
M	Moderate	Trace Impurity
W	Weak	
VW	Very weak	
T	Trace	
FT	Faint trace	
--	Not detected	

TABLE III. - IRRADIATION OF VARIOUS COPPER SALT SOLUTIONS

[Copper salt concentration: 0.1M; 1.0M methanol; 2 MeV electrons; Beam current: 10 uA; Dose: 0.030 coulomb.]

Salt	Product	Yield, n·G(M)	Reaction
CuSO_4	Cu	4.4	$2\text{Cu}^+ \longrightarrow \text{Cu}^0 + \text{Cu}^{+2}$
$\text{Cu}(\text{ClO}_4)_2$	Cu	4.4	$2\text{Cu}^+ \longrightarrow \text{Cu}^0 + \text{Cu}^{+2}$
$\text{Cu}(\text{OOCCH}_3)_2$	Cu_2O	4.4	$2\text{Cu}^+ + 2\text{OH}^- \longrightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$
CuCl_2	Cu_2Cl_2	4.4	$2\text{Cu}^+ + 2\text{Cl}^- \longrightarrow \text{Cu}_2\text{Cl}_2$
$\text{CuSO}_4 + 1\text{M NH}_3$	$\text{Cu}(\text{NH}_3)_x^+$	—	$\text{Cu}^+ + x\text{NH}_3 \longrightarrow \text{Cu}(\text{NH}_3)_x^+$
$\text{Cu}(\text{NO}_3)_2$	Cu	.6	$\left. \begin{array}{l} \text{NO}_3^- + e_{\text{aq}}^- \\ \text{NO}_3^- + \text{H}\cdot \end{array} \right\} \longrightarrow \text{reduction products}$

TABLE IV. - EFFECT OF ORGANIC ADDITIVES ON

n·G(Cu) FROM IRRADIATED AQUEOUS CuSO_4

[Electron energy: 2 MeV; CuSO_4 concentration: 0.2M; Beam current: about 10uA]

Additive	Additive concentration, m/l	Dose, coulomb	n·G(Cu)
Formaldehyde	1.0	0.030	4.4
Methanol	1.0	.030	4.4
Formic acid	1.0	.030	3.2
Ethanol	1.0	.030	4.2
2-propanol	1.0	.030	3.8
Glycerine	1.0	.030	4.4
Tetrahydrofuran	1.0	.030	4.0
Mannitol	.5	.030	4.4
Acetonitrile	1.0	.030	0
Acetic acid	1.0	.12	.05
Acetone	1.0	.10	.08
2-propyn-1-ol	1.0	.10	0
Methylethyl ketone	1.0	.030	.54
Pyrogallol	.5	.10	.12

TABLE V. - EFFECT OF ORGANIC ADDITIVES ON

n·G(Ni) FROM IRRADIATED AMMONIACAL NiSO_4

[Electron energy: 2 MeV; Beam current:
 20 μA ; Dose: 0.18 coulomb; NiSO_4 concen-
 tration: 0.2M; NH_3 concentration: 2.0M.]

Additive	Concentration, m/l	n·G(Ni)
2-propanol	1.0	1.76
1-butanol	1.0	.48
Ethanol	1.0	.44
Methanol	1.0	.40
Tetrahydrofuran	1.0	.32
Mannitol	.5	.08
2-methyl-2-propanol	1.0	.06
Formaldehyde	1.0	<.01
Acetone	1.0	<.01
Glycerine	1.0	<.01
2-propyn-1-ol	1.0	<.01
Sodium hypophosphite	.5	>20.0

TABLE VI. - YIELD OF METAL FROM IRRADIATION OF AQUEOUS METAL

SALT SOLUTIONS WITH 2 MeV ELECTRONS

0.1M metal salt	Metal yield, n·G(M); (valence change)· (atoms/100 eV)		
	CH ₃ OH concentration: 1M; current: 20 μ A; dose: 0.12 coulomb	Basic; NH ₃ conc: 1M unless specified	
		2-propanol con- centration: 1M; current: 20 μ A; dose: 0.12 coulomb	NaH ₂ PO ₂ concen- tration: 0.5M; current: 5 μ A; dose: 0.02 coulomb
AgClO ₄	3.6	3.0	
ZnSO ₄	.04	.008	0.006
Zn(OOCCH ₃) ₂	.28		
CdSO ₄	.90	.60	.70
Cd(OOCCH ₃) ₂	1.8		
TlOOCCH ₃	.13	.79	4.4
SnCl ₂	.20	^a .20	^a 1.0
Pb(ClO ₄) ₂	2.3		
Pb(OOCCH ₃) ₂	3.2	^a 3.0	^a 3.0
SbCl ₃	.26	^{a,b} 2.7	^a 5.1
CoSO ₄	.04	^c .60	^c .05
Co(OOCCH ₃) ₂	.06		
FeSO ₄	0	^d .001	^d .001
PdCl ₂	4.7		

^aNaOH added, no NH₃ present.^bCH₃OH added, no 2-propanol present.^cAlso 0.1M in (NH₄)₂SO₄.^dAlso 0.25M in citric acid.

TABLE VII. - SELECTIVE DEPOSITION

Initial solution	Precipitate
0.1M CuSO_4 , 0.1M NiSO_4 , 0.25M H_2SO_4 , 1.0M CH_3OH	Cu (20 ppm Ni)
0.1M CdSO_4 , 0.1M ZnSO_4 , 1.0M NH_3 , 1.0M 2-propanol	Cd (Zn <100 ppm)

TABLE VIII. - CODEPOSITION OF COBALT AND NICKEL

Initial solution: 0.1M NiSO_4 , 0.1M CoSO_4 , 0.1M (NH_4) $_2\text{SO}_4$, 1.0M NH_3 , 1.0M 2-propanol		
Consecutive runs on same initial solution, run number	Total metal precipitated in each run, percent	Composition of precipitate, percent Co
1	10.3	94
2	13.9	90
3	15.7	90
4	19.3	46
5	9.4	8
6	9.3	7
7	7.5	7

Final solution: 0.023M Ni^{+2} and 0.006M Co^{+2}

TABLE IX. - YIELD OF ANTIMONY UPON IRRADIATION

OF SbCl_3 SOLUTIONS IN DRY ORGANIC LIQUIDS

[Electron energy: 2 MeV; SbCl_3 concentration: 0.25M; Current: 20 μA ; Dose: 0.20 coulomb.]

Organic liquid	n·G(Sb)	Purity of Sb, percent
Methanol	2.4	99.9+
1-butanol	1.9	99.9+
Tetrahydrofuran	1.9	98.6
2-propanol	1.6	99.0
Amyl acetate	.73	94.6
Quinoline	.40	
Dibutyl phthalate	.35	
2-methyl-2-propanol	.32	
Oleic acid	.30	
Toluene	.25	About 85
Ethylbenzene	.25	About 90
Acetic acid	.20	
3-heptanone	0	
Glycerol	0	

TABLE X. - PREPARATION OF ANHYDROUS

HALIDES OF METALS IN A LOWER

OXIDATION STATE

Starting solution	Precipitate
FeCl_3 + tetrahydrofuran	FeCl_2
FeCl_3 + toluene	FeCl_2
CuBr_2 + 1-butanol	Cu_2Br_2
TiCl_4 + toluene + heptane	TiCl_3

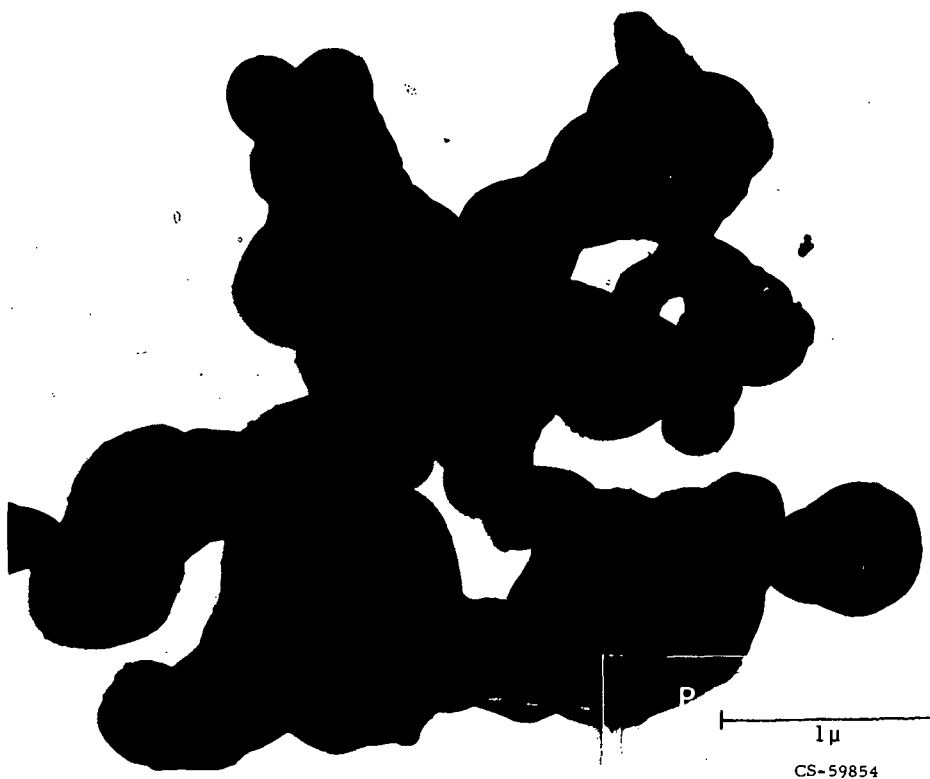
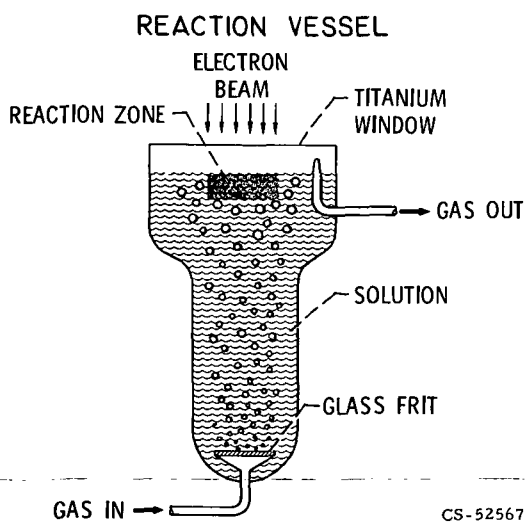


Fig. 1. - Photomicrograph of silver metal powder.



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Fig. 2

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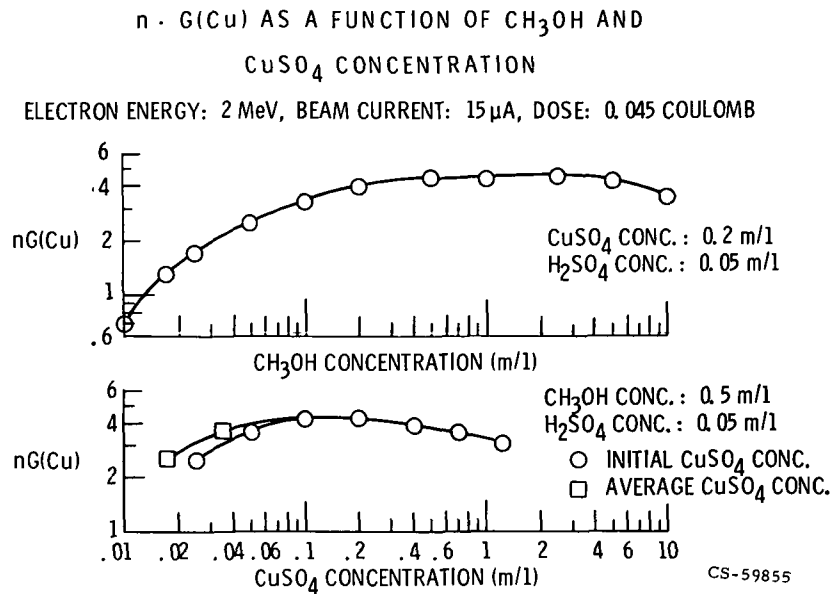


Fig. 3

EFFECT OF SbCl_3 CONCENTRATION IN TETRAHYDROFURAN
ON ANTIMONY YIELD

ELECTRON ENERGY: 2 MeV, CURRENT: 20 μA ,
DOSE: 0.20 COULOMB

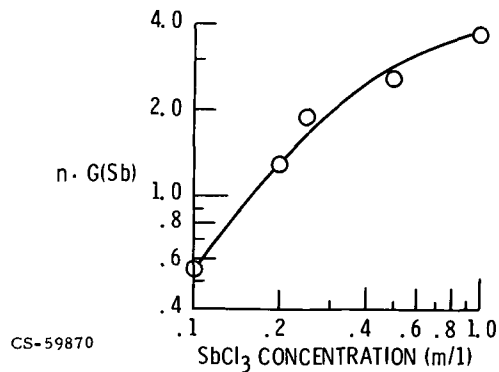


Fig. 4